

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61M 25/00, 25/10, C08G 69/48	A1	(11) International Publication Number: WO 98/55171 (43) International Publication Date: 10 December 1998 (10.12.98)
(21) International Application Number: PCT/US98/09257		(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 6 May 1998 (06.05.98)		
(30) Priority Data: 08/867,362 2 June 1997 (02.06.97) US		Published <i>With international search report.</i>
(71)(72) Applicant and Inventor: ACQUARULO, Lawrence, A., Jr. [US/US]; 329 Lake Road, P.O. Box 997, Dayville, CT 06241 (US).		
(72) Inventor: O'NEIL, Charles, J.; 5 Lancaster Avenue, Chelmsford, MA 01824 (US).		
(74) Agent: GROSSMAN, Steven, J.; Hayes, Soloway, Hennessey, Grossman & Hage, 175 Canal Street, Manchester, NH 03101 (US).		

(54) Title: CROSS-LINKED NYLON BLOCK COPOLYMERS

(57) Abstract

A cross-linked nylon block copolymer comprising a copolymer containing a polyamide block and an elastomeric block, irradiation cross-linked, including a compound which promotes cross-linking therein. In process form, the present invention comprises supplying a nylon block copolymer, containing a polyamide block and an elastomeric block, along with cross-linking promotor and exposing the block copolymer to irradiation, sufficient to cross-link the copolymer and improve mechanical properties therein. The cross-linked nylon block copolymers here have particular utility in both the medical and wire and cable industries.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

1 **CROSSLINKED NYLON BLOCK COPOLYMERS**

2 The present invention relates to the preparation of crosslinked nylon block
3 copolymer materials, and to their use in medical applications, particular as a
4 component for the preparation of a rigidized stem section for a catheter or other
5 similar medical device. In addition, the crosslinked nylon block copolymer materials
6 herein have utility in the wire and cable industry.

7 Generally, nylon block copolymers may be alternating blocks of polyamide
8 segments and other segments such as segments of elastomeric polymers such as
9 polyethers, polyesters, hydrocarbons or polysiloxanes. These nylon block copolymers
10 are generally prepared by copolymerizing a lactam monomer in the present of the
11 elastomeric polymers component. A more detailed discussion of the structure and
12 method of preparing particular types of nylon block copolymers can be found in U.S.
13 Patent No. 4,031,164.

14 The polyamide segments and elastomeric polymer segments of the nylon
15 block copolymers each contribute to the respective properties of the final polymer. In
16 order to obtain high modulus materials, polyamide segments of higher molecular
17 weight and/or higher weight percent can be employed. Alternatively, greater tensile
18 elongation and impact properties, as well as lower surface hardness, may be obtained
19 by using higher percents of and/or higher molecular weight elastomeric polymer
20 component.

21 U.S. Patent No. 4,671,355 appears to be one of the first disclosures of a
22 crosslinked nylon block copolymer, chemically, through the use of polyfunctional
23 amine compounds. That is, the crosslinked nylon block copolymers are prepared by a
24 reaction scheme in which polyfunctional amines act as crosslinking agents. More
25 specifically, a crosslinked material was reportedly synthesized by reacting an acyl
26 lactam functionalized material with the polyfunctional amine to prepare crosslinked
27 acyl lactam materials which were then concurrently or subsequently reacted with
28 lactam monomer in the presence of a lactam polymerization catalyst to form the
29 crosslinked nylon block copolymer material. It was reported therein that by
30 chemically crosslinking, it was discovered that the overall properties of the final

1 polymer could be varied even if one maintains the molecular weight and weight
2 percent of the elastomeric polymer component.

3 While the above chemical method of crosslinking a nylon block copolymer
4 has been reported, no reports exist concerning the development of a nylon block
5 copolymer by a more convenient method such as irradiation. The closest attempts in
6 this regard can be found, for example, in Plast. Massy, 1993, No. 2, pp 35-37, which
7 contains a paper entitled "Production and Properties of Crosslinked Compositions of
8 Aliphatic Nylons". According to the abstract, a study was conducted on the process
9 of radiation crosslinking of an aliphatic polyamides (i.e., not a nylon block
10 copolymers) and an assessment is made of the properties and network compositions
11 obtained. The materials studied were nylon-6, nylon-6,6 and nylon-12. The
12 polyfunctional monomers employed to accelerate crosslinking were triallyl cyanurate
13 and triallyl isocyanurate. Mechanical data is supplied.

14 Similarly, in the Chinese Journal of Polymer Science, Vol. 7, No. 1, there is a
15 paper entitled "Characterization of Irradiated Crystalline Polymer-Isothermal
16 Crystallization Kinetics of Radiation Induced Crosslinked Polyamide 1010". As
17 disclosed therein, after irradiation, the service temperature of the resin is raised to
18 about 240 °C. In addition, network formation is said to greatly change the
19 crystallization behavior of the otherwise crystalline polyamide material.

20 Finally, it is worth noting that various other disclosures have been uncovered,
21 which recite thermoset (or crosslinked) polyamide resins, but again, no mention or
22 suggestion of irradiation crosslinking of a nylon block copolymer is described. For
23 example, in U.S. Patent No. 5,198,551 entitled "Polyamide Thermosets" there is
24 disclosed what is termed curable polyamide monomers, curable liquid crystal
25 polyamide monomers and thermoset compositions prepared therefrom. The
26 thermoset polyamides so prepared all contained highly aromatic type structure.
27 Similarly, in U.S. Patent No. 5,3154,011, which is a divisional of the '551 Patent,
28 there is again described curable polyamide monomer systems, which monomers
29 represent highly aromatic type functionality.

1 The fact that there have been no reports concerning the development of a
2 convenient route for the preparation of a crosslinked nylon block copolymer is
3 underscored when reference is made to U.S. Patent No. 5,584,821, which discloses an
4 angiographic catheter which has a relatively stiff though flexible shaft and a soft tip.
5 The soft tip consists primarily of a tungsten loaded polyether block amide (PEBA)
6 copolymer surrounded by two thin PEBA layers. This three ply radiopaque tip is
7 bonded to a PEBA shaft. The shaft is reinforced either by an inner nylon ply or by
8 metal braiding.

9 In other words, pursuant to the teachings of U.S. Patent 5,584,821 when it
10 comes to the production of a soft tip catheter with a relatively stiffer body, the
11 teachings therein emphasize that the stiffer body portion relies upon the use of a metal
12 braided reinforced PEBA copolymer or a co-extruded two ply wall consisting of nylon
13 and PEBA copolymer. That being the case, it becomes clear that inasmuch as PEBA
14 type copolymers are widely used in catheter type applications, it would serve a long-
15 standing need if one could conveniently produce a more rigid and toughened PEBA
16 catheter, without the need for the structural modifications emphasized in the prior art.

17 Accordingly, it is an object of this invention to prepare a crosslinked nylon
18 block copolymer, wherein said polymer is conveniently crosslinked by the process of
19 irradiation or other high energy source, wherein such crosslinked nylon block
20 copolymer has particular utility as a component of a medical catheter product.

21 More specifically, it is object of the present invention to prepare a crosslinked
22 nylon block copolymer elastomeric formulation, via irradiation techniques, wherein
23 the elastomeric composition, subsequent to crosslinking, exhibits improvement in
24 properties such as mechanical strength, heat resistance, and hardness, and in
25 particular, the crosslinked material so produced demonstrates elongational behavior
26 when exposed to elevated temperatures under conditions of constant stress.

27 Furthermore, it is an object of the present invention to crosslink nylon block
28 copolymer systems, wherein such crosslinking improves the overall elastomeric
29 toughness of the block copolymer, thereby providing what can be termed a much

1 more durable nylon block copolymer product for a variety of miscellaneous
2 applications in the medical industry.

3 A crosslinked nylon block copolymer comprising a copolymer containing a
4 polyamide block and an elastomeric block, irradiation crosslinked, including a
5 compound which promotes crosslinking therein. In process form, the present
6 invention comprises supplying a nylon block copolymer, containing a polyamide
7 block and an elastomeric block, along with crosslinking promotor and exposing said
8 block copolymer to irradiation, sufficient to crosslink said block copolymer and
9 improve mechanical properties therein, particularly the ability of said block
10 copolymer to elongate upon exposure to a constant load of about 29 psi (2039
11 gm/cm²) at an elevated temperature of about 200 °C for 15 min.

12 As noted above, the present invention in composition form relates to a an
13 irradiation-crosslinked nylon block copolymer . Preferably, the nylon block
14 copolymer is a nylon block copolymer sold by ATOCHEM under the tradename
15 PEBA^X® which is a elastomeric type nylon block copolymer. The commercial
16 PEBA^X polymers consist of polyether blocks separated by polyamide blocks. The
17 polyether blocks may be based upon polyethylene glycol, polypropylene glycol, or
18 polytetramethylene ether glycol. The polyamides are usually based upon nylon-11 but
19 may be based upon nylons 6 of nylon-6,6 or even a copolymer such as nylon-6/nylon-
20 11. A wide range of block polyamides have been offered and vary in the type of
21 polyether, the nature of the polyamide block and the ratio of polyether to polyamide
22 blocks. The polymers range in hardness from Shore A 60 to Shore D72 which is
23 broader than for the thermoplastic polyester and thermoplastic polyurethane rubbers.
24 Melting range is also dependent on the particular composition, and varies between
25 140 - 215 °C.

26 The above nylon block copolymers have been found to undergo crosslinking
27 upon exposure to irradiation. Listed below in Table I are the results of various
28 exposure levels as applied to a PEBA^X Shore 72A material, containing 2.0% TAIC
29 (triallylisocyanurate) and the corresponding changes in mechanical properties
30 observed:

1

TABLE I

	0 MR	5 MR	10MR	15MR	20MR
T.S. (psi)	8,632	10,531	7,751		
(g/cm ²)	606,890	740,403	544,959		
Yield (psi)	4,026	4,979	5,186		
(g/cm ²)	283,056	350,059	346,612		
100% Mod (psi)	3,498	4,035	4,216		
(g/cm ²)	245,934	283,689	296,414		
Elong (%)	*404.2	*358.3	*283.3	**	**
Creep (%)	***	54.3	61.4	58.3	63.0
Set (%)	--	1.5	4.1	3.6	4.6

2

3 * = Necked

4 ** = NOTE: The 15mr and 20mr samples necked and there was very little
5 elongation (less than 0.635 cm.).6 *** At 200 °C, the unexposed material melted. At 150 °C the unexposed
7 material elongated 0.0794 cm. (3.1%). At 175 °C it broke in the clamp, but did not
8 melt. The sample elongated 1.5875 cm. (62.5%) before it broke.9 One of the more relevant properties reported on in Table I, is the % Creep
10 which was measured at 200 °C, 29 psi (2,039 gm/cm²), over a 15 minute period. This
11 is formally known as the "Test Method for Measurement of Hot Creep of Polymeric
12 Insulations", Publication T-28-562, published by the Insulated Cable Engineers
13 Association, Inc, of South Yarmouth, Massachusetts. In accordance with the present
14 invention, elongations of less than 100% are preferred, and most preferred is an
15 elongation of about 10-65%.16 As can be seen, unexposed PEBAK actually melted under these conditions of
17 testing, and no elongation was observed. By contrast, after a 5 megarad total
18 exposure, the percent creep is about 54.6%. In other words, irradiation clearly
19 promotes crosslinking and network formation within the nylon block copolymer

1 material, and as a thermoset, it no longer melts and flow, and elastomeric behavior is
2 observed.

3 Also, as can be seen from Table I, exposure to 5 megarads results in an
4 associated drop in the percent of elongation from about 404 % to about 358 %, which
5 is a characteristic expected due to crosslinking. In addition, exposure at 5 megarads
6 increases the tensile strength from about 8600 psi (604,640 gm/cm²) to about 10,500
7 psi (738,224 gm/cm²) , which is again a result of network crosslink formation.

8 As can also be seen in Table I, while an exposure of 5 megarads along with
9 about 2.0 % of a promotor ("TAIC" or "TAC", triallylcyanurate) provides optimum
10 composition and conditions, higher exposure levels are still acceptable. For example,
11 a total exposure of 10 megarads similarly provides a sample that elongates about 61 %
12 after exposure to 29 psi (2,039 gm/cm²) , at 200 °C for 15 minutes. However, with
13 respect to this particular sample, it is worth pointing out that the tensile strength drops
14 to about 7750 psi (544,879 gm/cm²) , which may be the onset of some degradation.
15 Upon exposure to even higher total levels of irradiation (15 and 20 megarads) the
16 sample still demonstrates elongational values of about 58 and 63 %, respectively,
17 however, at such total exposure levels, the samples necked and their was very little
18 elongation at room temperature. Again, this is believed to be the result of the
19 degradation that may take place when total irradiation becomes too high.

20 With regards to the specific utility of the invention disclosed herein, it is noted
21 that the crosslinked nylon block copolymer disclosed herein has utility in both the
22 medical products field, as well as in the wire and cable industry.

23 More specifically, when it comes to the production of an intravascular flexible
24 catheter having a tubular shaft comprising a nylon block copolymer, and a soft
25 flexible tubular tip distal of and bonded to said shaft, the improvement recited herein
26 comprises irradiation crosslinking said nylon block copolymer of said shaft, wherein
27 said crosslinking increases the rigidity of said shaft relative to said soft flexible distal
28 tip. In addition, in the balloon catheter field, in the case of such catheters
29 manufactured from a nylon block copolymer, the invention herein provides for the
30 preparation of a balloon type catheter, wherein the balloon section relative to the shaft

1 can be converted into a thermoset or crosslinked type structure, thereby increasing its
2 overall mechanical strength, performance, and durability.

3 Accordingly, the compositions and method disclosed herein provide a much
4 more convenient route for the preparation of a novel rigid-flex nylon block copolymer
5 resin, particularly suited for the production of novel type catheter products, without
6 the need for structural modification of the catheter type systems as disclosed and
7 emphasized by the prior art. In addition, the compositions herein are well-suited as
8 an electrical insulating material for the wire and cable industry.

CLAIMS

2 1. A crosslinked nylon block copolymer comprising a copolymer
3 containing a polyamide block and an elastomeric block, irradiation crosslinked,
4 including a compound which promotes crosslinking therein.

5 2. The crosslinked nylon block copolymer of claim 1 wherein said
6 crosslinked nylon block copolymer elongates after about 15 minutes at about 200 °C
7 and about 29 psi (2,039gm/cm²).

8 3. The crosslinked nylon block copolymer of claim 2 wherein said
9 elongation is less than about 100 %, and preferably is about 10-65 %.

10 4. The crosslinked nylon block copolymer of claim 1, wherein said
11 elastomeric block is selected from a polyether, polyester, hydrocarbon, polysiloxane,
12 or mixtures thereof.

13 5. The crosslinked nylon block copolymer of claim 1, wherein said
14 compound which promotes crosslinking is triallylisocyanurate or triallylcyanurate.

15 6. The crosslinked nylon block copolymer of claim 5, wherein the
16 triallylisocyanurate or triallylcyanurate is present at a level of about 2.0 % (wt).

17 7. The nylon block copolymer of claim 1, wherein said irradiation is less
18 than about 20 megarads, and preferably 5, 10 15 or 20 megarads.

19 8. In an intravascular flexible catheter having a tubular shaft comprising a
20 nylon block copolymer, and a soft flexible tubular tip distal of and bonded to said
21 shaft, the improvement comprising irradiation crosslinking said nylon block
22 copolymer of said tubular shaft, wherein said crosslinking increases the rigidity of
23 said shaft relative to said soft flexible distal tip.

24 9. In a balloon type catheter having a tubular shaft comprising a nylon
25 block copolymer and an integrally formed balloon section, the improvement
26 comprising irradiation crosslinking said nylon block copolymer of said balloon
27 section, wherein said crosslinking lowers the percent elongation of said balloon
28 section as compared to the elongation prior to crosslinking.

29 10. A process for preparing a crosslinked nylon block copolymer
30 comprising supplying a copolymer containing a polyamide block and an elastomeric

- 1 block, mixing a crosslinking promotor into said copolymer, and exposing said
- 2 copolymer with promotor to irradiation crosslinking.

INTERNATIONAL SEARCH REPORT

International application No. PCT/US98/09257

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61M 25/00, 25/10; C08G 69/48
 US CL :522/137; 523/421, 426; 604/93, 96, 280

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 522/137; 523/421, 426; 604/93, 96, 280

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,617,355 (GABBERT et al.) 14 October 1986, see entire document.	1-4, 7
A	US, A, 5,584,821 (HOBBS et al.) 12 December 1996, see abstract.	8, 9
A	US, A, 4,444,816 (RICHARDS et al.) 24 April 1984, see abstract.	1-7, 10

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"		document defining the general state of the art which is not considered to be of particular relevance
"B"		earlier document published on or after the international filing date
"L"		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"		document referring to an oral disclosure, use, exhibition or other means
"P"		document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search

07 JULY 1998

Date of mailing of the international search report

11 AUG 1998

Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231
 Facsimile No. (703) 305-3230

Authorized officer

 PATRICIA SHORT
 Telephone No. (703) 308-2351